

Kremer-Grest models for universal properties of specific common polymer species

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Abstract

The Kremer-Grest (KG) bead-spring model is a near standard in Molecular Dynamic simulations of generic polymer properties. It owes its popularity to its computational efficiency, rather than its ability to represent specific polymer species and conditions. Here we investigate how to adapt the model to match the universal properties of a wide range of chemical polymers species. For this purpose we vary a single parameter originally introduced by Faller and Müller-Plathe, the chain stiffness. Examples include polystyrene, polyethylene, polypropylene, cis-polyisoprene, polydimethylsiloxane, polyethyleneoxide and styrene-butadiene rubber. We do this by matching the number of Kuhn segments per chain and the number of Kuhn segments per cubic Kuhn volume for the polymer species and for the Kremer-Grest model. We

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also derive mapping relations for converting KG model units back to physical units, in particular we obtain the entanglement time for the KG model as function of stiffness allowing for a time mapping. To test these relations, we generate large equilibrated well entangled polymer melts, and measure the entanglement moduli using a static primitive-path analysis of the entangled melt structure as well as by simulations of step-strain deformation of the model melts. The obtained moduli for our model polymer melts are in good agreement with the experimentally expected moduli.

1 Introduction

Polymers are long chain molecules built by covalent linkage of a large numbers of identical monomers.^{1,2} Some properties of polymeric materials such as their density or glass transition temperature depend on chemical details at the monomer scale. Others, like the variation of the melt viscosity with the molecular weight of the chains, are controlled by the large scale chain statistics.³ These properties, which are characteristic of polymeric systems, are universal^{4,5} in that they are shared by large numbers of chemically different systems.

The character of the target properties is crucial for the choice of a model in theoretical or computational investigations. Universal properties can be studied using simple, numerically convenient lattice and off-lattice models, see e.g. refs.^{6–8} for reviews. In contrast, predicting specific materials properties for a given chemical species requires atom-scale modeling.⁹ A growing body of work aims at developing coarse-grained models^{10–14} designed for specific polymer chemistries, for example in the case of polyethylene,^{15–17} polyisoprene,^{18–21} polystyrene,^{22,23} polyamide,^{24,25} polydimethylsiloxane,^{26,27} polymethacrylate,^{28,29} bisphenol-A polycarbonate,^{30–33} polybutadiene,^{34,35} polyvinyl,³⁶ polyterephthalate,³⁷ and polyimide.³⁸ Common to these approaches is the selected inclusion of specific chemical details. These models offer insights into which atomistic details of the chemical structure are relevant for particular non-universal polymer properties and perhaps also allow for transferability to a larger domain of state space.^{13,39}

In the present paper, we use a more theory-inspired route to including specificity, which re-

quires experimental input on the local equilibrium chain structure and dynamics. From universality, we expect that by matching a very limited number of microscopic length and time scales,⁴⁰ we can 1) design generic polymer models that match the properties of real chemical polymers, and 2) map the predictions of such simulations back to experiment. In contrast to theoretical approaches and without needing to be accurate on the atomic scale, a properly mapped generic polymer model should automatically reproduce many non-trivial static and dynamic features such as correlation holes, as well as stress relaxation via constraint release and contour length fluctuations.^{3,41} Generic models allow for the investigation of effects due to polymer branching, chain polydispersity, and/or chemical cross-linking, see^{42–45} for examples. Generic models not only reproduce the properties of bulk polymer materials, but also films, tethered polymer chains, spatially confined polymers materials, welding of polymer interfaces or composite materials formed by adding filler particles to a polymer melt or solid, see^{46–55} for examples.

The KG model is used in a vast number of publications as a basis for studying generic polymer and materials physics, see e.g.^{7,8,13} for reviews. In this model approximately hard sphere beads are connected by strong non-linear springs. The spring potential is chosen to energetically prevent two polymer chains from passing through each other, allowing to sample entangled dynamics.⁵⁶ It can be mapped to experimental systems^{40,57} by adjusting the chain stiffness via a local bending potential.^{58–60} Compared to lattice models, the deformation response of polymer materials can be straightforwardly studied by deforming the simulation domain e.g. via shear,^{61,62} uniaxial^{63,64} or biaxial elongation without worrying about artifacts introduced by a underlying lattice.

We apply this philosophy to the most popular Molecular Dynamics polymer model introduced by Kremer and Grest (KG).^{56,65} Here we use KG models of varying stiffness to model real polymers species. We generate huge well equilibrated melt states using a new equilibration process.⁶⁶ We predict the plateau modulus from the model melts using the Primitive-path analysis⁶⁷ and stress-relaxation after step-strain and compare results to experimental values.

The paper is structured as follows; We present the relevant theory in Sec. 2, the Kremer-Grest model and its mappings to real polymers is introduced and characterized in Sec. 3. We present our

results for the plateau moduli for KG models of real polymers in Sec. 4, and conclude with our conclusions in Sec. 5.

2 Theory

Before introducing the Kremer-Grest model and how to map it to a given chemical polymer species, we introduce the basic quantities used to characterize static and dynamic properties of polymer melts and in particular their dependence on the number of Kuhn segments per cubic Kuhn length. This will be the central quantity that we want to reproduce by our KG model systems.

2.1 Chain and melt structure

At a given state point, a long monodisperse polymer melt is characterized by just a few experimental observables: the molecular mass of a polymer chain M_c , the mass density ρ_{bulk} , the average chain end-to-end distance $\langle R^2 \rangle$, the contour length of the chains, L , and the maximal intra-chain relaxation time, τ_{max} .

From these experimental observables we can derive a set of microscopic parameters characterizing the melt, such as the chain number density, $\rho_c = \rho_{bulk}/M_c$, its inverse, the volume per chain, $V_c = 1/\rho_c$, and the Kuhn length,

$$l_K = \frac{\langle R^2 \rangle}{L} \quad (1)$$

which is the fundamental length scale characterizing chain configurations beyond the monomer scale. The number of Kuhn segments per chain is

$$N_K = \frac{\langle R^2 \rangle}{l_K^2} = \frac{L^2}{\langle R^2 \rangle} \quad (2)$$

and the mass and density of Kuhn segments are given by $M_K = M_c/N_K$ and $\rho_K = V_K^{-1} = N_K/V_c$ respectively.

There are various manners to characterize the mutual chain interpenetration in polymer melts. The Flory number,

$$n_F = \rho_c \langle R^2 \rangle^{3/2} = (\rho_K l_K^3) N_K^{1/2}, \quad (3)$$

is defined as the number of chains populating, on average, the volume spanned by one chain. For a given polymer material, the Flory number increases with the square root of the chain length, since $\rho_c \propto N_K^{-1}$ and $R \propto N_K^{1/2}$. The chemistry-specific prefactor in this relation is the reduced Kuhn density,

$$n_K = \rho_K l_K^3, \quad (4)$$

defined as the number of Kuhn segments within a cubic Kuhn length. In most melts of flexible polymers we have $1 \leq n_K \leq 10$, whereas in gels of tightly entangled filamentous proteins such as f-actin we have $n_K \gg 10$.⁶⁸ To define a length scale characterizing the chain packing in a polymeric material, one can consider a spherical region centered on a chosen monomer. If the region is small, then most monomers found inside will belong to the same chain as the chosen monomer. On the other hand, if the region is large, then most monomers inside the region will belong to other chains. The packing length,^{69,70}

$$p = \frac{V_c}{\langle R^2 \rangle} = (l_K^2 \rho_K)^{-1} = \frac{l_K}{n_K}, \quad (5)$$

defines the crossover between these two regimes. It corresponds to the root-mean square end-to-end distance of polymers with Flory number $n_F \equiv 1$ and $N_K = 1/n_K^2$.

2.2 Local dynamics

The dynamics of short unentangled polymers is described by the Rouse model.⁷¹ In this model a single Gaussian polymer is modeled by a chain of Kuhn segments, and the dynamics is modeled by Brownian motion with a friction term describing the mean field friction due to the surrounding chains. In polymer melts, hydrodynamic interactions are strongly screened and can be neglected. From the Rouse model, the fundamental Kuhn time is given by

$$\tau_K = \frac{\zeta_K l_K^2}{3\pi^2 k_B T}. \quad (6)$$

This is time that it takes a single Kuhn segment to diffuse ($D_K = k_B T / \zeta_K$) its own size. The Kuhn friction or equivalently the Kuhn time sets the fundamental time scale of all dynamical polymer properties. The maximal internal relaxation time of a chain with N_K Kuhn units is given by the Rouse time $\tau_R = \tau_K N_K^2$ and the melt viscosity is predicted to be $\eta = \zeta_K N_K / (36 l_K)$.⁷¹

2.3 Predicting emergent large scale dynamics and rheological behaviour

While chains undergoing Brownian motion can slide past each other, but their backbones cannot cross.³ As a consequence, the motion of long chains is subject to transient topological constraints,⁷² an effect which is familiar from the manipulation of knotted strings. These constraints become relevant at scales beyond the entanglement (contour) length,^{70,73} L_e , or the equivalent the number of Kuhn units between entanglements, $N_{eK} = L_e / l_K$. For loosely entangled polymers, entanglements contribute to the linear elastic response on the level of the entanglement modulus

$$\frac{G_e l_K^3}{k_B T} = \frac{\rho_K l_K^3}{N_{eK}} = \frac{n_K^3}{\alpha^2}. \quad (7)$$

In this limit,⁶⁸ there are

$$N_{eK} = \left(\frac{\alpha}{n_K} \right)^2 \quad (8)$$

Kuhn segment per entanglement length. The (spatial) tube diameter is given by

$$\frac{d_T}{l_K} = \sqrt{\frac{\langle R^2(N_{eK}) \rangle}{l_K^2}} = \sqrt{N_{eK}} = \frac{\alpha}{n_K} \quad (9)$$

while

$$\tau_e = \tau_K N_{eK}^2 = \tau_K \left(\frac{\alpha}{n_K} \right)^4. \quad (10)$$

defines the corresponding entanglement time.

The relevance of the packing length,

$$d_T = \alpha p, \quad (11)$$

to the microscopic topological state can be understood through the primitive path analysis (PPA).^{40,67,68}

The numerical prefactor (see also fig. 2), describes the number of entanglement strands per entanglement volume^{74,75}

$$\alpha = \frac{\rho_K}{N_{eK}} d_T^3 \quad (12)$$

and appears to be a universal constant for all flexible polymers. A geometric argument⁷⁶ suggests $\alpha = 20.49$ for the local pairwise entanglement of Gaussian chains.⁷⁷ The analysis of large experimental data sets for polymers at $T = 413K$ and $T = 298K$ yielded $\alpha = 19.36$ and $\alpha = 17.68$ respectively.⁷⁸

Modern theories of polymer dynamics and rheology³ describe the universal aspects of the viscoelastic behavior based on the idea that molecular entanglements confine individual filaments to a one-dimensional, diffusive motion (reptation⁷⁹) in tube-like regions in space.⁸⁰ In the long chain limit, the maximal relaxation time is⁷⁹

$$\tau_{max} = 3 \left(\frac{N_K}{N_{eK}} \right)^3 \tau_e. \quad (13)$$

In slowing down the chain equilibration after a deformation, entanglements dominate the viscoelastic behavior of high molecular weight polymeric liquids. For $\tau_e < t < \tau_{max}$ the shear relaxation modulus, $G(t)$ exhibits a rubber-elastic plateau, $G_N = \frac{4}{5}G_e$, of the order of the entanglement modulus, increasing the melt viscosity to

$$\eta = G_e \tau_{max} \sim \frac{N_K^3}{N_{eK}^2}. \quad (14)$$

As illustrated by this brief outline of (linear) melt viscoelasticity, two polymeric systems char-

acterized by the same number of Kuhn segments, N_K , and the same dimensionless Kuhn density, n_K , (and hence identical numbers of entanglements $Z = N_K/N_{eK}$) are expected to show the same universal large scale behavior. By matching the Kuhn length, l_K , and the Kuhn time, τ_K , and by measuring energy in units of the thermal excitation energy, $k_B T$, results obtained for one system can be converted into predictions for the other.

This analogy is not restricted to experimental systems, but also extends to computational models provided they preserve the key features of polymer melts: chain connectivity, local liquid-like monomer packing, and the impossibility of chain backbones to dynamically cross through each other. Nor is the analogy restricted to the linear viscoelasticity of monodisperse melts of linear chains, but should hold more generally provided the two systems are characterized by comparable amounts of branching, polydispersity, or cross-linking. Even without being accurate on the atomic scale, a properly mapped simulated model should automatically reproduce many non-trivial static and dynamic features (e.g. correlation holes,⁴¹ contour-length fluctuations, constraint release, and dynamic dilution effects^{3,81}) which are difficult to preserve in theoretical approaches.

2.4 The choice of the contour length

Before proceeding, it is useful to briefly reflect on the importance of the choice of the contour length, L , for the emergent properties of the coarse-grain model. In other words, what changes, if we choose a different contour length, $L' = \lambda L$, for the mapping? By construction, this choice modifies the Kuhn length and all quantities associated with it:

$$\begin{aligned} l'_K &= \frac{\langle R^2 \rangle}{L'} = \frac{l_K}{\lambda} \\ N'_K &= \frac{L'}{l'_K} = \lambda^2 N_K \\ \rho'_K &= \rho_c N'_K = \lambda^2 \rho_K \\ n'_K &= \rho'_K l'^3_K = \frac{n_K}{\lambda} \end{aligned}$$

However, on first sight, this seems to have no consequences for the quantities discussed in the preceding section: the Flory number,

$$n'_F = n'_K N_K'^{1/2} = n_F , \quad (15)$$

the packing length,

$$p' = \frac{l'_K}{n'_K} = p , \quad (16)$$

the tube diameter

$$d'_T = \left(\frac{l'_K}{n'_K} \right) \alpha = d_T \quad (17)$$

and the entanglement modulus,

$$\frac{G'_e}{k_B T} = \left(\frac{n'_K}{l'_K} \right)^3 \alpha^{-2} = \frac{G_e}{k_B T} \quad (18)$$

appear to remain unaffected. What does change, however, are ratios like

$$N'_{eK} = \frac{L'_e}{l'_K} = \left(\frac{d'_T}{l'_K} \right)^2 = \left(\lambda \frac{d_T}{l_K} \right)^2 = \lambda^2 \frac{L_e}{l_K} = \lambda^2 N_{eK} . \quad (19)$$

The number of Kuhn segments per entanglement strand, N'_{eK} , defines the maximal elongation of entanglement strands and is relevant for the non-linear viscoelastic response of strongly elongated melts and networks³ as well as craze formation in glassy polymers.^{82,83} But even for modelling linear viscoelasticity, L' and hence N'_{eK} , cannot be chosen freely, at least if the model is meant remain in the loosely entangled regime. Flexible chain behaviour on the entanglement scale requires, that the Kuhn length be smaller than the tube diameter: $1 \ll d'_T/l'_K$ or $N'_{eK} \gg 1$. If this is the only constraint, then the computationally most efficient approach is to choose a (relatively stiff) model, where $n'_K \approx \alpha/2$ close to the crossover to the tightly entangled regime.^{84,85} In the remainder of the article we employ a physically realistic choice of the contour length to parameterize coarse-grain

models, which can be used to explore larger deformations.

3 Model and Mapping

3.1 Kremer-Grest model

The Kremer-Grest (KG) model^{56,65} is a quasi-standard in Molecular Dynamics investigations of generic polymer properties. The KG model is a bead-spring model, where the mutual interactions between all beads are given by the Weeks-Chandler-Anderson (WCA) potential (the truncated and shifted repulsive part of the 12-6 Lennard-Jones potential),

$$U_{WCA}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{-12} - \left(\frac{\sigma}{r} \right)^{-6} + \frac{1}{4} \right] \quad \text{for } r < 2^{1/6}\sigma, \quad (20)$$

while bonded beads interact through the finite-extensible-non-linear spring (FENE) potential given by

$$U_{FENE}(r) = -\frac{kR^2}{2} \ln \left[1 - \left(\frac{r}{R} \right)^2 \right]. \quad (21)$$

We choose $\varepsilon = k_B T$ and σ as the simulation units of energy and distance, respectively. The standard choices for the Kremer-Grest model is to set $R = 1.5\sigma$ and $k = 30\varepsilon\sigma^{-2}$. We also choose the standard number of beads per unit volume $\rho_b = 0.85\sigma^{-3}$. Here and below we use subscript “b” to denote bead properties to distinguish these from Kuhn units used above. With these choices, the bond length becomes $l_b = 0.965\sigma$. We add an additional bending interaction defined by

$$U_{bend}(\Theta) = \kappa(1 - \cos \Theta), \quad (22)$$

where Θ denotes the angle between subsequent bonds. The stiffness parameter κ controls the Kuhn length l_K and the reduced Kuhn density n_K of the resulting polymer model. The same potential has previously been studied by Faller and Müller-Plathe.^{58–60} For other choices, see Ref.⁸⁶

For integrating the dynamics of the KG model we use Langevin dynamics

$$m_b \frac{\partial^2 \mathbf{R}_i}{\partial t^2} = -\nabla_{\mathbf{R}_i} U - \Gamma \frac{\partial \mathbf{R}_i}{\partial t} + \xi_i(t) \quad (23)$$

where \mathbf{R}_i denotes the position of bead i and U the total potential energy. $\xi_i(t)$ is a Gaussian distributed random vector with $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t) \cdot \xi_j(t') \rangle = \frac{6k_B T}{\Gamma \Delta t} \delta(t - t') \delta_{ij}$. The mass of a bead is denoted m_b , and we choose this as our mass scale for the simulations. From the currently defined units we can derive a simulation unit of time $\tau = \sigma \sqrt{m_b / \varepsilon}$. We use the standard Kremer-Grest choice of $\Gamma = 0.5 m_b \tau^{-1}$ for the friction of the Langevin thermostat together with integration time steps $\Delta t = 0.01 \tau$. For integrating the dynamics of our systems, we use the Grønbech-Jensen/Farago Langevin integration algorithm as implemented in the Large Atomic Molecular Massively Parallel Simulator (LAMMPS).^{87–89}

Before we can generate KG models of specific polymers, we need to characterize the Kremer-Grest model in terms of the dependency of the Kuhn length and the Kuhn friction on the chain stiffness κ .

3.2 Kuhn length

It is difficult to predict the Kuhn length of a polymer model directly from the microscopic force field. While excluded volume interactions are approximately screened in melts (the Flory ideality hypothesis⁹⁰), the incompressibility constraint of melts leads to deviations from polymer Θ -solutions via a correlation hole, which causes the chain stiffness to increase due to a long range effective repulsive interaction between polymer blobs.^{41,91–95}

Here we brute force equilibrate medium length entangled melts with $M = 2000$ chains of length $N_b = 400$ for varying chain stiffness. Each initial melt conformation was simulated for at least $2 \times 10^5 \tau$ while performing double-bridging hybrid Monte Carlo/Molecular Dynamics simulations.^{15,16,96,97} Configurations from the last $5 \times 10^4 \tau$ of the trajectory were used for analysis. We chose $N = 400$, since the chains are long enough to estimate the Kuhn length (see below) without compromising the efficiency of the double-bridging algorithm.

The Kuhn length is estimated using

$$l_K = \frac{\langle R^2(N_b) \rangle}{N_b \sqrt{\langle l_b^2 \rangle}} = 2\sqrt{\langle l_b^2 \rangle} \int_0^{N_b} \left(1 - \frac{n}{N_b}\right) C(n) dn, \quad (24)$$

where $C(n) = \langle \mathbf{b}(m) \cdot \mathbf{b}(m+n) \rangle_m$ is the bond correlation function averaged along the contour of the chain. The result is shown in Fig. 1. As expected, the Kuhn length increases with the bending stiffness. The simulation data are well fitted by a cubic polynomial, which allows us to obtain the chain stiffness parameter k required to reproduce a desired Kuhn length $l_K(\kappa)$. For $l_K > 7\sigma$, KG polymer melts undergo a isotropic-nematic phase transition,⁵⁸ however the present systems are in the isotropic state.

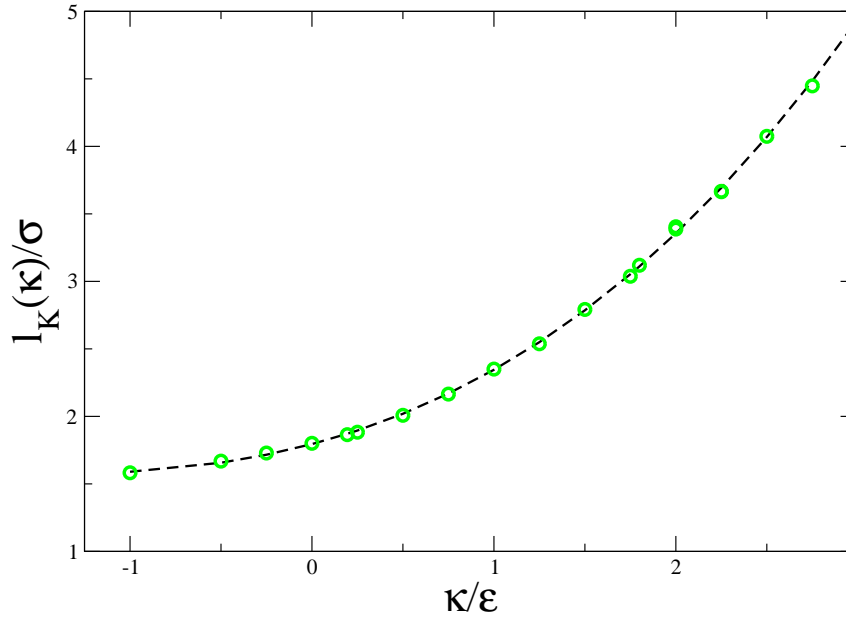


Figure 1: Kuhn length l_K vs stiffness parameter κ for Kremer-Grest polymer model (green symbols), also shown is an interpolation given by $l_K(\kappa)/\sigma = 1.795 + 0.358\epsilon^{-1}\kappa + 0.172\epsilon^{-2}\kappa^2 + 0.019\epsilon^{-3}\kappa^3$ (hashed black line).

3.3 Primitive-path analysis

To estimate the entanglement length as function of chain stiffness, we have generated highly entangled melt states with $M = 500$ chains of length $N_b = 10000$ for stiffness parameter $\kappa = -1, -0.5, 0, 0.5, 1.0, 1.5, 2.0, 2.5$. The details of the equilibration procedure can be found in Ref.⁶⁶ We have performed primitive-path analysis (PPA) of the melt states. During the primitive path analysis a melt conformation is converted into the topologically equivalent primitive-path mesh work characterizing the microscopic topological melt state.⁶⁷ During the analysis the chain ends are fixed, hence the mean-square end-to-end distance is constant.

The Kuhn length of the tube is given by $a_{pp} = \langle R^2 \rangle / L_{pp}$ where L_{pp} is the average contour length obtained from the primitive-path mesh. Here we distinguish between the tube diameter d_T predicted by rheology and a_{pp} predicted from the static PPA analysis, even though these two parameters describes the same physics, and are expected to be the same on a scaling level. Hence we can obtain the number of Kuhn segments between entanglements as $N_{eK}(\kappa) = a_{pp}(\kappa) / l_K^2(\kappa)$. We have performed a version of the PPA analysis that preserves self-entanglements by only disabling pair interactions between beads within a chemical distance of $2N_{eK}$. Subsequently the potential energy was minimized. The minimization was performed using the steepest descent algorithm implemented in LAMMPS followed by dampened Langevin dynamics. We have used the method of Hoy et al.⁹⁸ to check for finite chain length effects, however, this can be completely neglected for all the the chain lengths used here.

Fig. 2 shows the chain stiffness dependence of the entanglement length. As expected as the chain become stiffer, their spatial size increases, and hence also the number of entanglements. This leads to the observed reduction in the distance between entanglements. The inset shows the theoretical prediction based on the universal number of $\alpha = 18.0$ chains per entanglement volume, which is in very good agreement with the simulation results.

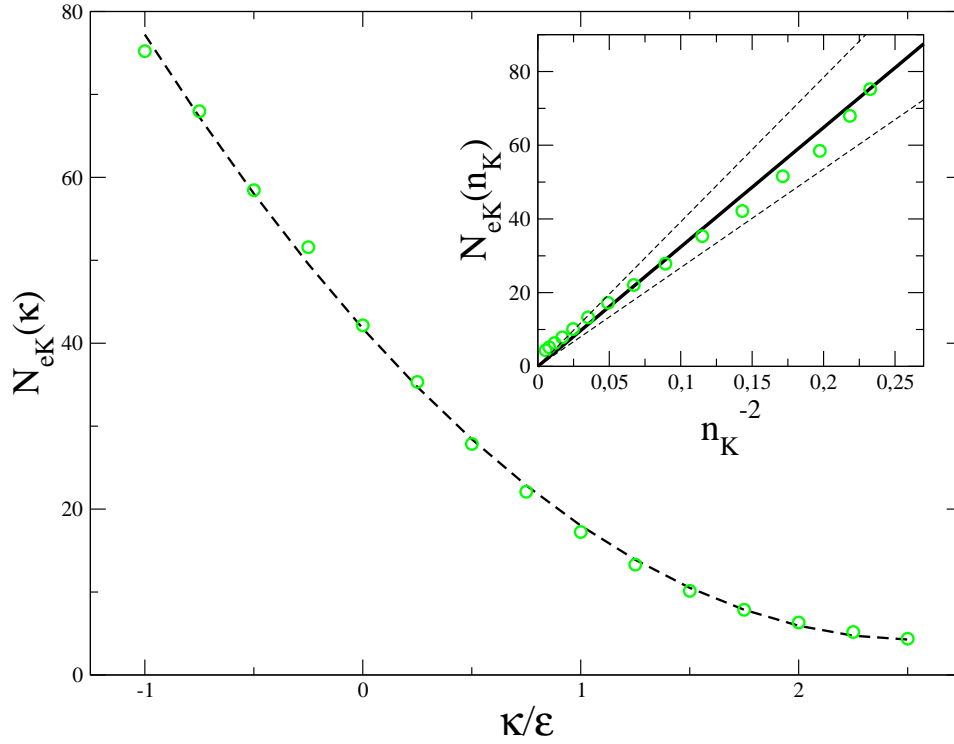


Figure 2: Entanglement length N_{eK} vs stiffness parameter for Kremer-Grest polymer model (green symbols). The inset shows the same data but as function of the reduced Kuhn density. Shown is an interpolation given by $N_{eK}(\kappa) = 41.774 - 29.605\epsilon^{-1}\kappa + 5.842\epsilon^{-2}\kappa^2$ (hashed black line) and the theoretical relation $N_{eK}(n_K) = \alpha^2 n_K^{-2}$ with $\alpha = 18.0$ (solid black line in the inset with hashed lines indicating a $\pm 10\%$ error).

3.4 Time mapping

To define a relevant time scale for the polymer dynamics, we measure the Kuhn friction ζ_K . For short chains $N_K < N_{eK}(\kappa)$, Rouse theory applies, and the Kuhn friction can be obtained by

$$\zeta_K(\kappa) = \frac{k_B T}{D_{cm}(\kappa, N_K) N_K}. \quad (25)$$

We have performed a series of simulations of melts of 2000 chains of length $N_K = 3, 4, 5, 8, 10, 15, 20, 30$, which were equilibrated for a period of $10^4 \tau$ using double bridging hybrid MC/MD^{15,16,96,97} as above. The resulting equilibrium melt states were run for up to $2 - 10 \times 10^5 \tau$ and the center of mass diffusion coefficient $D_{cm}(\kappa, N_K)$ was obtained from the plateau of $\langle [R_{cm}(t) - R_{cm}(0)]^2 \rangle / [6t]$ for $t > 10^5 \tau$ by sampling plateau values for log-equidistant times, and discarding simulations where the standard deviation of the samples exceeded 2% of their average value.

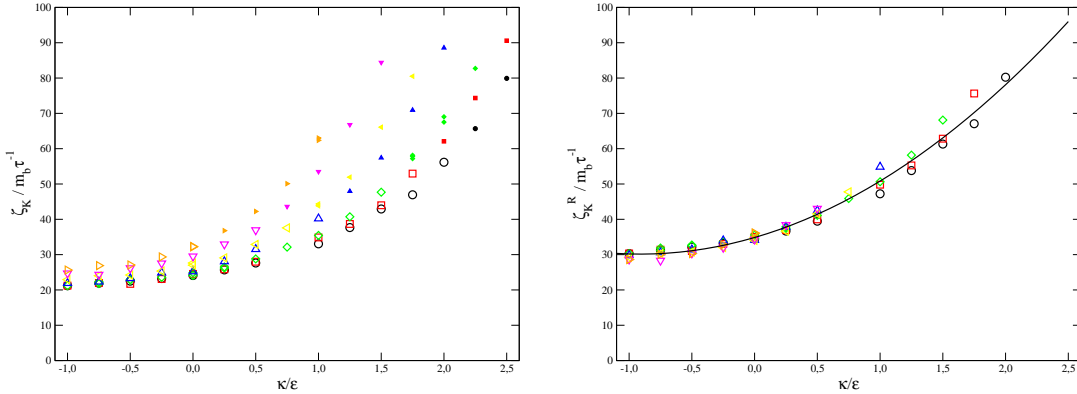


Figure 3: Kuhn friction ζ_K (top) and renormalized friction ζ_K^R (bottom) vs stiffness parameter. The friction was estimated from simulations with $N_K = 3, 4, 5, 8, 10, 15, 20, 30$ (black circle, red box, green diamond, blue triangle up, yellow triangle left, magenta triangle down, orange triangle right, respectively). Simulations where the Rouse model is expected to be valid ($N_K < N_{eK}(\kappa)/2$) are shown with large open symbols, the rest are shown with small closed symbols. Shown is also a trend line given by $\zeta_K(\kappa)/[m_b \tau^{-1}] = 34.85 + 10.31(\kappa/\epsilon) + 5.659(\kappa/\epsilon)^2$ (solid black line).

Fig. 3 shows the Kuhn friction obtained from the analysis of the simulations using eq. (??). We observe that the friction increases with stiffness for all chain lengths, but most strongly for the long chains. This is to be expected since spatial size of the chains increase, and hence more strongly confine the diffusive dynamics. The Rouse model should apply for chains that are shorter

than the entanglement length (open symbols in the figure), and we would expect these to collapse to a single line, however we see a systematic and significant spread in the simulation data. This is due to larger mobility of beads towards the chain ends compared to beads far away from the chain ends. We have corrected for this by defining a renormalized Kuhn Friction

$$\zeta_K^R(\kappa) = \zeta_K(\kappa)g(N_K), \quad (26)$$

where the g function describes the chain-length dependence of the reduction of friction due to chain ends. Opting for simplicity, we use a linear interpolation where N_{end} Kuhn segments have friction reduced by a factor f_{end} while the friction due to the rest of the Kuhn segments is unaffected, hence

$$g(N_k) = \begin{cases} f_{end} & \text{for } N_K < N_{end} \\ N_K^{-1}((N_K - N_{end}) + f_{end}N_{end}) & \text{for } N_K \geq N_{end} \end{cases}. \quad (27)$$

The parameters were determined by minimizing the variance between Kuhn friction estimates where 1) the Rouse model applies and where 2) we have at least three values estimates for the friction. We obtained $f_{end} = 0.70$ and $N_{end} = 7$, which corresponds to completely neglecting the friction due to the outermost Kuhn segment at each end. This choice reduced the total variance of the renormalized frictions by more than an order of magnitude. The result is shown in Fig. 3, where we observe an significantly improved collapse of the data allowing us to estimate the effective Kuhn friction required for the time mapping of long entangled chains. Note that since the entanglement length drops rapidly for large stiffnesses ($N_{eK}(2.5\varepsilon) < 5$), it is not possible to perform simulations where chains are long and the Rouse model applies at the same time. This necessitates a renormalization procedure that resolves the end effect.

Experimentally observable is the entanglement time $\tau_e(\kappa) = \tau_K(\kappa)N_{eK}^2(\kappa)$. Empirical relations for the chain stiffness dependent entanglement and Kuhn times are shown in Fig. 4. The Kuhn time rises steeply with increased chain stiffness, since the friction itself rises steeply with stiffness. This is most likely due to the fact that as chains become stiffer they interact with more chains. This

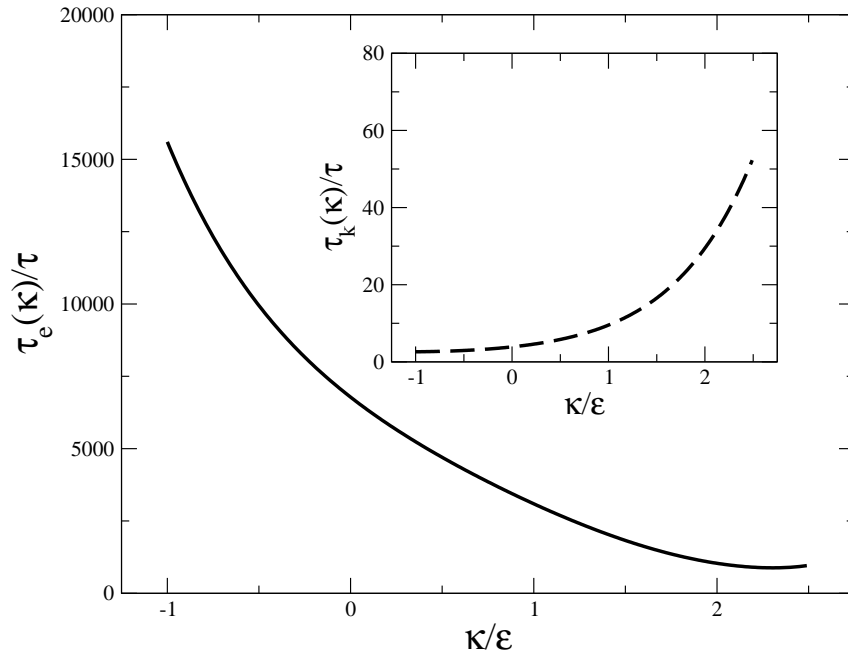


Figure 4: Entanglement time $\tau_e(\kappa)$ and Kuhn time $\tau_K(\kappa)$ in KG units as function of stiffness parameter predicted using the interpolations given in figs. 1, 2, and 3.

slows down the dynamics, which we rationalize as an apparent increase in the friction coefficient felt by the center-of-mass. On the other hand, since the entanglement length drops with stiffness the net effect is that the entanglement time drops with increasing chain stiffness.

Time mappings have previously been studied for the standard KG model ($\kappa = 0$) Likhtman⁹⁹ obtained $\tau_e(\kappa = 0) \approx 5800\tau$ by fitting shear-relaxation moduli produced by KG simulations, while Kremer and Grest¹⁰⁰ obtained $\tau_e(\kappa = 0) = 1.5N_{eb}^2$ from Rouse mode analysis of chain dynamics. Here $N_{eb} = c_b N_{eK}$ denotes the entanglement length expressed in beads. Using the most recent value for the entanglement length $N_{eb} = 85 \pm 7$ ⁹⁸ results in $\tau_e(\kappa = 0) = 10800 \pm 1800\tau$. However, looking into the data of Kremer and Grest more carefully, they also give an effective bead rouse friction of $\zeta_b = 25 \pm 2m_b\tau^{-1}$, and using the relations in the present paper to derive an estimate for the entanglement time results in a somewhat reduced entanglement time of $\tau_e(\kappa = 0) = 8800 \pm 700\tau$. Our present result $\tau_e(0) = 6780\tau$ is in reasonable good agreement with both Likhtman and our refined Kremer and Grest value.

3.5 Mapping

Given a specific chemical polymer species characterized by its Kuhn length l_K , and reduced density of Kuhn segments n_K . We would like to design a Kremer-Grest model and a mapping that reproduces these properties. This gives rise to the following equations

$$c_b(\kappa)l_b \equiv l_K, \quad (28)$$

and

$$c_b^2(\kappa)l_b^3\rho_b = l_K^3(\kappa)\rho_K(\kappa) \equiv n_K. \quad (29)$$

Here we have the physical quantities on the right hand side, and the corresponding KG expressions on the left hand side. Hence from the second equation we learn the numerical value of $c_b(\kappa)$ which is dimensionless, while from the first equation we learn the mapping the KG length unit to

the real physical unit of the Kuhn length. The physical interpretation of these two equations is that they provide the number of beads per Kuhn segment as well as the width of the beads required to fulfill the constraints.

Given a concrete number of molecules with N_K Kuhn segments per molecule, we can generate a corresponding initial state with $N_b = c_b(\kappa)N_K$ beads per chain and M such chains in the volume required to produce the target density ρ_b . What remains is to map the simulation results back to real physical units specific for the chosen polymer species. With the energy scale set to the (target) thermal excitation energy, $\varepsilon = k_B T$, all that remains to be done is to fix the bead mass m . Equating the masses of the Kuhn segments,

$$c_b(\kappa)m_b \equiv M_K. \quad (30)$$

This is a one parameter family of KG polymer models, since we keep the density fixed and adjust only a single parameter, the chain stiffness κ , to the specific polymer species. We expect this to work well for dense polymer melts, however, modeling dilute or semi-dilute solutions would require KG models where we also adapt the density of beads to match the volume fraction of monomers, and perhaps also modify the bead interactions to take solvent induced effects into account. These additional complexities are outside the scope of the present paper.

With this present approach different polymer species with matching pairs of l_K and n_K are mapped unto the same KG model. Recently Zhang et al. presented an similar approach,¹⁰¹ where a given polymer species was represented by KG models varying both the stiffness and density, where the mapping was based on keeping the Flory number $n_F = N_K^{3/2}M^{-1} \times n_K$ constant. Equilibrated low-resolution precursor melts was rescaled and successively fine grained to reach the resolution of a target model as determined. Here take as a starting point a real specific polymer chemistry, and derive a corresponding KG polymer model varying only the stiffness while retaining the standard density. We also produce a set of mapping relations for units. We subsequently generate an equilibrated melt for this model using a fast multiscale equilibration procedure that we recently developed.⁶⁶

In table 1 we summarize the relevant experimental and chemical properties of eight chosen

polymers. These are the numbers that are required to define equivalent KG models. In Tab. 2 we characterize the same polymers in terms of Kuhn and entanglement properties required. As expected the reduced Kuhn densities varies within $1 \leq n_K \leq 10$. Note that the average ratio of the tube diameter to the packing parameter is approximately a universal constant $\alpha = \langle d_T/p \rangle = 18.0 \pm 1.3$ for all the polymers.

Table 1: Polymer properties: Reference temperature T_{ref} , end-to-end distance per molecular weight $\langle R^2 \rangle / M_c$, bulk mass density ρ_{bulk} , monomer mass, and back bone contour length per monomer. The physical properties are from Ref.¹⁰² ¹SBR rubber has 25% styrene content.

	T_{ref}/K	$\frac{\langle R^2 \rangle}{M_c} / [\text{\AA}^2 \text{mol}/g]$	$\rho_{bulk} / [g/cm^3]$	$M_m / [g/mol]$	$l_m / \text{\AA}$
PDMS	298	0.422	0.970	74.15	3.30
cis-PI	298	0.679	0.910	68.12	4.96
a-PP	298	0.678	0.852	42.08	3.08
a-PS	413	0.437	0.969	104.15	3.08
PEO	353	0.805	1.06	44.05	4.40
SBR ¹	298	0.818	0.913	66.59	4.09
PE413	413	1.25	0.785	28.05	3.08
PE298	298	1.40	0.851	28.05	3.08

Table 2: Descriptions of polymers in terms of Kuhn length l_K , reduced Kuhn density n_K , monomers per Kuhn length c_∞ , packing length p , and the dimensionless ratio of tube diameter d_T and the packing length. The tube diameter was derived using the experimental plateau moduli in Tab. 5.

	$l_K / \text{\AA}$	n_K	c_∞	$p / \text{\AA}$	d_T / p
PDMS	9.48	2.34	2.87	4.06	15.7
cis-PI	7.76	2.89	1.30	2.69	17.1
a-PP	9.26	3.22	3.01	2.87	17.0
a-PS	14.78	3.77	4.80	3.92	19.5
PEO	8.06	4.14	1.83	1.95	17.1
SBR	13.34	6.00	3.26	2.22	19.6
PE 413	11.38	6.73	3.70	1.69	19.0
PE 298	12.76	9.15	4.14	1.39	18.6

3.6 Kremer-Grest models of common polymers

Using the relations presented above, we have generated Kremer-Grest model parameters and mappings for the eight chosen polymer species shown in Tab. 1, the mapping relations are shown in

Tab. 3. From the mapping relations, we note that the only free parameter, the stiffness parameter varies from $\kappa = -0.36$ up to $\kappa = 2.0$, which falls into the range where our empirical relations for Kuhn length, entanglement length, and Kuhn friction are valid. The number of beads per monomer produced by the mapping is about 1 ± 0.5 . The length scale of the beads is around $5 \pm 2\text{\AA}$, the energy scale is by construction always kT . Despite fairly small variations in the length and energy scales, the unit of stress $\varepsilon\sigma^{-3}$ is seen to be quite sensitive to the specific polymer species.

Based on our time mappings, we can estimate the Kuhn and entanglement times for the polymers, which can be compared directly to results obtained from rheology or neutron spin-echo scattering to provide a time mapping. For example, for PDMS the entanglement time is $\tau_e(288K) = 1.0 \times 10^{-6}s$,¹⁰³ and for cis-PI $\tau_e(298K) = 13.21 \times 10^{-6}s$,¹⁰⁴ based on these values we obtain time mappings $1\tau = 0.1 - 2.4ns$. Hence the simulation time steps $\Delta t = 0.01\tau$ corresponds to $\approx 10^4 fs$, secondly due to the number of atoms represented by a single bead, the coarse-graining alone gives factor of ten speed increase. Hence simulations with the KG models are about 10^5 times faster than atomistic simulations of the same polymer. However, the time mapping should by no means be assumed valid for other polymer species or state points, especially if the reference temperature is close to the glass transition temperature. In such cases the speedup of the present approach for representing the large scale behaviour is exponentially larger, since the standard KG model without attractive interactions does not exhibit a glass transition.¹⁰⁵

Table 3: Kremer-Grest models and unit mappings for the polymers shown in Tab. 1 and 2.

	κ/ε	c_b	M_m/m_b	m_b/amu	$\sigma/\text{\AA}$	$\varepsilon/10^{-21}J$	$\varepsilon\sigma^{-3}/MPa$	τ_K/τ	τ_e/τ
PDMS	-0.357	1.749	0.609	121.80	5.617	4.114	23.21	3.07	8650
cis-PI	0.206	1.944	1.493	45.62	4.136	4.114	58.15	4.42	5710
a-PP	0.429	2.054	0.683	61.62	4.673	4.114	40.31	5.35	4861
a-PS	0.710	2.221	0.463	224.97	6.894	5.702	17.40	6.98	3923
PEO	0.866	2.328	1.271	34.65	3.587	4.874	105.63	8.19	3448
SBR	1.417	2.802	0.858	77.58	4.932	4.114	34.30	15.0	2005
PE413	1.576	2.968	0.803	34.94	3.975	5.702	90.78	18.0	1672
PE298	1.988	3.461	0.836	33.55	3.818	4.114	73.93	29.3	1057

We have generated a single equilibrated melt sample for each of the polymer models in Table 3. We chose the chain length such that the number of entanglements per chain $Z = N_k/N_e \approx 100$, and

number of molecules such that the total number of beads in the system was approximately 5×10^6 . This ensures that the resulting systems are in the strongly entangled regime. For comparison the largest systems that were equilibrated with the recent method of Zhang et al.^{101,106} contained 2×10^6 beads and $Z = 24$ entanglements. The resulting melt states are listed in Tab. 4. Also shown in the table are estimates of their Rouse and maximal relaxation times.

Each melt state was equilibrated using a new computationally very fast method, that we have developed.⁶⁶ To summarize the process; lattice melts states were initially generated using a lattice chain model where blobs belonging to different polymers can occupy the same lattice site. The lattice Hamiltonian contains a term that penalizes density fluctuations,¹⁰⁷ and the large-scale chain statistics was equilibrated using Monte Carlo simulated annealing. The resulting lattice melt states were fine grained to a bead-spring polymer model, which was then further equilibrated at short and intermediate using a KG force field but with a force capped pair-interaction. This models allows some overlap between beads, and the resulting Rouse dynamics allows the lattice artifacts to be equilibrated while further reducing density fluctuations. Finally, the melt states were energy minimized with the KG force field and reheated to the standard temperature $T = 1\varepsilon$. We choose the number of molecules to produce a target systems with 5×10^6 beads, but self-consistently adjusted the number of molecules to minimize a round off introduced due to the lattice used in the first stage of the equilibration process. As a result the actual number of beads vary from 2.1×10^6 to 8.0×10^6 for aPS and cis-PI respectively. The reason for the variation of Z is that we used preliminary simulation results from shorter melts to provide an $N_e(\kappa)$ estimate. We have subsequently recalculated Z with the more accurate estimate obtained from the long entangled melts presented above.

4 Results and discussion

Having generated well-equilibrated melt configurations for our KG models shown in tab. 4, we now proceed to calculate their emergent rheological properties and to compare the results to ex-

Table 4: Prepared Kremer-Grest melt states. M number of molecules, Z number of entanglements per chain, N_K number of Kuhn units per chain, N_b number of beads per chain, τ_R Rouse time, and τ_{max} maximal relaxation time.

	M	Z	N_K	N_b	$\tau_R/10^7\tau$	$\tau_{max}/10^{10}\tau$
PDMS	303	108	5711	9990	10.0	3.23
cis-PI	939	122	4396	8547	8.55	3.14
a-PP	521	116	3486	7159	6.50	2.25
a-PS	289	141	3349	7438	7.83	3.32
PEO	1315	105	2155	5018	3.80	1.20
SBR	1076	117	1348	3777	2.73	0.96
PE413	1459	108	1037	3078	1.94	0.63
PE298	2219	90	543	1881	0.86	0.23

periment.

We have performed primitive-path analysis (PPA) of the melt states. During the primitive path analysis a melt conformation is converted into the topologically equivalent primitive-path mesh work characterizing the tube structure.⁶⁷ From the mesh work we can estimate the plateau modulus as

$$G_N^{est} = \frac{4\rho_K k_B T}{5N_{eK}} = \frac{4\rho_K k_B T l_K^2}{5a_{pp}^2}. \quad (31)$$

The numerator is specified by the polymer model and the mapping of units, while PPA provides the required Kuhn length of the primitive path. During the analysis the chain ends are fixed. The mean-square end-to-end distance is constant, and hence the Kuhn length of the tube is given by $a_{pp} = \langle R^2 \rangle / L_{pp}$ where L_{pp} is the average contour length obtained from the primitive-path mesh. The primitive-path analysis was performed as described above.

Table 5 shows the comparison between plateau moduli from experiments and those predicted by the primitive path analysis applied to the model polymer melts. Note that no rheological information was build into the KG models nor the mappings of units, hence this is a prediction of macroscopic elastic properties based solely on matching mesoscale conformational properties of the polymer molecules. We observe quite good agreement between most of the models and experimental values with five of the eight polymers being within 10% of the experimental value, and all

polymers are within 30% of the experimental plateau value. From this we can conclude that our melt states provide good descriptions of the true polymer melts properties, and secondly that our mapping of simulation to SI units is also correct.

Table 5: Comparison between predictions of experimental plateau moduli and moduli predicted from the primitive path mesh of the equilibrated polymer melt states.

	G_N^{exp}/MPa	G_N^{est}/MPa	G_N^{est}/G_N^{exp}
PDMS	0.20	0.172	0.86
cis-PI	0.58	0.580	1.00
a-PP	0.48	0.478	1.00
a-PS	0.20	0.251	1.26
PEO	1.8	1.703	0.95
SBR	0.78	0.813	1.04
PE413	2.6	2.451	0.94
PE298	3.5	2.500	0.71

Fig. 5 shows a comparison between the reduced experimental entanglement moduli of our polymers and the reduced plateau moduli produced by the KG models we can generate by varying the stiffness. The deviations we saw in Tab. 5 are completely consistent with the deviation between the experimental entanglement moduli and the KG model line. Almost all of the experimental values are within the 20% error interval around the KG models. The scatter observed between the experimental plateau moduli and the predicted plateau modulus line must be attributed either to chemical details causing some small degree of non-universal behaviour,¹⁰⁸ or to experimental uncertainties in accurately estimating the plateau modulus which can be quite difficult.¹⁰⁹ Nonetheless, the KG models are clearly able to predict the entanglement modulus of the chemical polymer species with good accuracy.

Also shown in Fig. 5 is a comparison between reduced plateau moduli of the KG models compared to the theoretical prediction eq. (??) using $\alpha = 18.0$ consistent with Fig. 2. The agreement is good for smaller values of n_K i.e. for flexible polymers, but increasingly deviate for stiffer polymers. A universal description for entanglement moduli of dense melts of flexible chains and tightly entangled gels of rigid rods was developed by Uchida et al.⁶⁸ The result was an extrapolation describing the reduced entanglement modulus using two free parameters, $c_\xi = 0.06$ and $c_G = 0.6$,

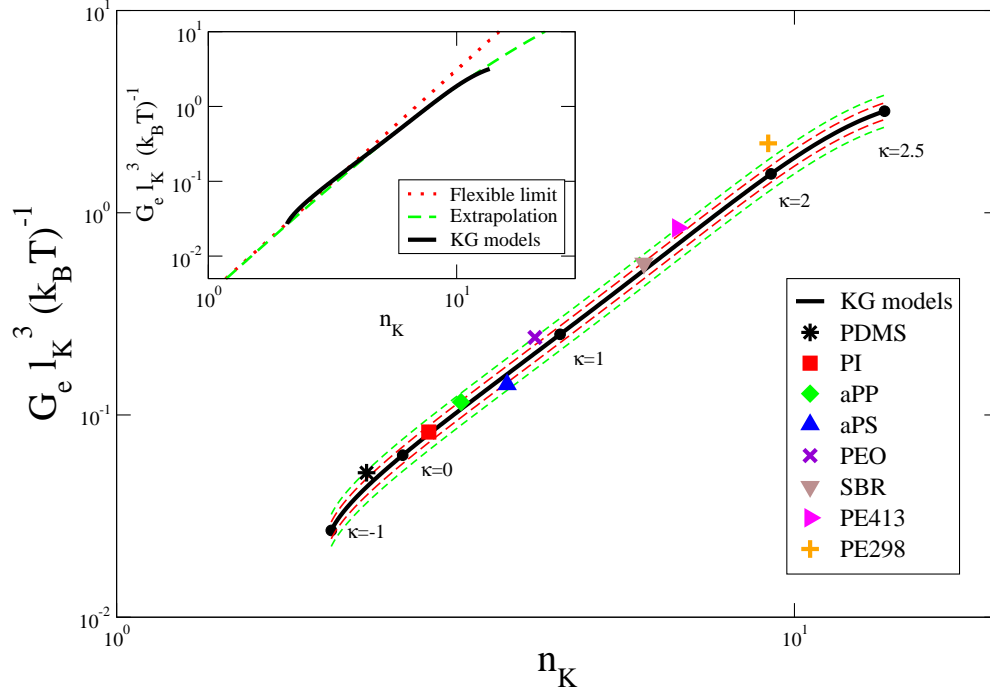


Figure 5: Reduced entanglement moduli for the chosen polymers (symbols), the one parameter family of KG models for the range of stiffness parameters $\kappa = -1, \dots, 2.5$ (solid black line) using the $N_{eK}(\kappa)$ interpolation from Fig. 2 including ten and twenty percent error intervals (red hashed and green hashed lines, respectively). The insert shows a comparison between KG reduced moduli, flexible chain relation eq. (??) with $\alpha = 18.0$ (red dotted line), and an extrapolation from Ref.,⁶⁸ see the text for details. (green hashed line).

that fixes the the modulus in the flexible chain and rigid rod regimes, respectively. We retain the latter parameter, but replace the former parameter by $c_\xi = 2/[\alpha\sqrt{5c_G}] = 0.064$ consistent with $\alpha = 18.0$ in the flexible chain limit. With this choice, eqs. (5-7) of Ref.⁶⁸ reduce to the simple extrapolation formula

$$\frac{G_e l_K^3}{k_B T}(n_K) = \frac{n_K^{7/5}}{4 \left(243 n_K^{-2} + 3 n_K^{-2/5} + 1 \right)^{4/5}}. \quad (32)$$

This expression is also shown in the Fig. 5 and is in excellent agreement with the reduced entanglement moduli produced by the KG models for all values of the reduced Kuhn density or equivalently chain stiffness.

To estimate the plateau modulus from a purely rheological approach, we have also performed rapid uniaxial step-strain simulations of some of the model melts. The deformation is followed by a long stress relaxation simulation at constant strain. We obtained the parallel and perpendicular stress components σ_{\parallel} and σ_{\perp} from the instantaneous microscopic virial tensor. The melts were strained by an elongation factor $\lambda = 1.5, 2.0, 3.0$ during a fast simulation of just $\Delta t = 10^2 \tau = 3 - 29 \tau_K$. These deformations are far inside the non-linear response regime for the polymer melts. The systems were then run $2 \times 10^5 \tau$ corresponding to $22 - 191 \tau_e$ or to $0.002 - 0.023 \tau_R$ at constant strain while the stress relaxed. The simulations should be long enough to see the onset of a stress plateau, but not long enough for the chains to contract to their equilibrium length, and certainly far too short to start seeing the terminal stress relaxation at τ_{max} . We thus expect to see stress relaxation to the level of the entanglement modulus rather than to the level of the plateau modulus.

The shear relaxation modulus $G(t)$ can be obtained from

$$\sigma_T(\lambda; t) = h(\lambda)G(t), \quad (33)$$

where $\sigma_T(\lambda; t) = \sigma_{\parallel} - \sigma_{\perp}$ is the normal tension, and $h(\lambda)$ is a damping function. The damping function describes the tube reorganization due to the applied strain as well as initial fast stress relaxation processes due to chain length redistribution inside the tube, which we do not expect to

be relevant for the present simulations..

Our ability to estimate the plateau modulus from the simulation data depends on having expressions for the damping function that takes into account the non-linear large-strain response of the polymer melts. Several expressions have been proposed based on different assumptions for the strain response of polymer melts. The classical damping function $h^{CL}(\lambda) = \lambda^2 - \lambda^{-1}$ is based on the assumption of affine deformations. Doi and Edwards (see Ref.³ eqs. 7.137-7.141) derived a time-dependent damping function, which includes a uniform contour length contraction dynamics of the chain inside an affine deforming strain independent tube mesh work. In the early time limit, where contour length contraction does not occur, this damping function reduce to

$$h^{DE}(\lambda) = \left(\frac{15\lambda^2(\lambda^3 + \frac{1}{2})}{16(\lambda^3 - 1)} \right) \left(\frac{\sinh^{-1}(\sqrt{\lambda^3 - 1})}{\sqrt{\lambda^3(\lambda^3 - 1)}} + 1 \right) \\ \times \left(1 - \frac{(4\lambda^3 - 1) \sinh^{-1}(\sqrt{\lambda^3 - 1})}{\sqrt{\lambda^3(\lambda^3 - 1)}(2\lambda^3 + 1)} \right) \quad (34)$$

Rubinstein and Panyukov¹¹⁰ derived a non-affine tube model, where the tube diameter is assumed to change with deformation as $d_T \sim \lambda^{1/2}$. This is believed to model the weaker tube localization effect of entanglements due to chain slipping compared to localization due to chemical cross-links, which is strain independent.^{111,112} This assumption gives rise to the following damping function for a melt

$$h^{RPNA}(\lambda) = \frac{\lambda^2 - \lambda^{-1}}{\lambda - \lambda^{1/2} + 1} \quad (35)$$

Later, Rubinstein-Panyukov additionally allowed for chain length redistribution inside the tube. Their slip-tube model¹¹³ predicts

$$h^{RPST}(\lambda) = \frac{\lambda^2 - \lambda^{-1}}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35} \quad (36)$$

Previously, we concluded that the Rubinstein-Panyukov slip-tube damping function gave the

best agreement to simulation results for step-strained KG melts by comparing to shear relaxation moduli estimated using a Green-Kubo approach.¹¹⁴ However, these results were obtained for KG melts that were significantly shorter than the present systems, furthermore the deformations were up to two orders of magnitude slower, and hence we would expect complete or at least partial relaxation of chain length inside the tubes after the deformation for these results.

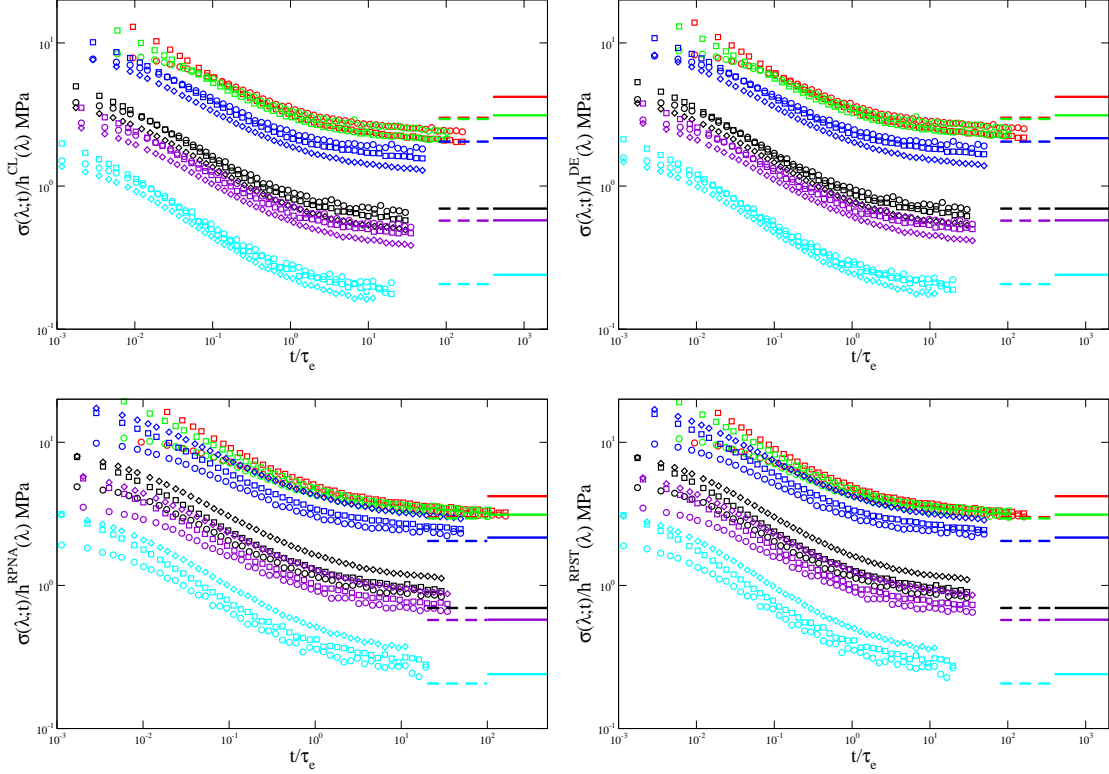


Figure 6: Shear relaxation modulus using the classical damping function (top left), the Doi-Edwards damping function (top right), and for the Rubinstein-Panyukov non-affine tube model (bottom left) and slip-tube (bottom right) for step-strains $\lambda = 1.5$ (circle), 2.0 (square), and 3.0 (diamond) for PDMS (cyan), aPP (violet), PI (black), PEO (blue), PE413 (green), PE298 (red). The experimental and PPA entanglement moduli are illustrated as horizontal solid and dashed lines, respectively.

Fig. 6 shows the shear relaxation modulus obtained using different damping functions. Also shown in the figure are the experimental entanglement moduli as well as moduli estimates from the primitive-path analysis. Since chain contraction occurs on much longer time scales than our simulations, we expect to measure the entanglement modulus rather than the plateau modulus. After an entanglement time τ_e , we observe that the modulus for each melt has dropped down and the start

of a plateau can be seen. Overall for all the damping functions we see a reasonable collapse of the data obtain from different strains. The classical and Doi-Edwards damping functions give rise to very similar shear relaxation moduli, that generally undershoot the expected entanglement moduli. Comparing the two theories of Rubinstein and Panyukov, we observe that they also give rise to very similar relaxation moduli, that are in better agreement with the experimental moduli than the classical and Doi-Edwards damping functions. This supports the validity of the assumption that the entanglement tube strain response is indeed sub-affine.¹¹⁵ Most importantly, the results suggests that we can indeed extract consistent moduli of our model materials from either the stress relaxation after a step-strain deformation or from the computationally much less expensive primitive path analysis.

5 Conclusion

We have shown how to model specific chemical polymer species with an extension of the Kremer-Grest polymer model introduced by Faller et al.⁵⁸ The force field has just a single adjustable parameter, the chain stiffness. By matching the Kuhn length and the reduced Kuhn density of the KG polymer model to the specific polymer, we can build KG melts of any flexible polymer species. Secondly we produce mapping relations converting simulation units to SI units, such that we can compare our predict macroscopic viscoelastic properties to the experimental values of the real polymers.

We have illustrated this approach by designing KG polymer models for eight standard polymer species of both commercial and academic interest. We have build well equilibrated massively entangled model polymer melts for these species, and measured the plateau moduli of the model melts using both primitive-path analysis (PPA) of the static conformations and extensive stress relaxation simulations after a rapid step-strain deformation. PPA seems to be the method of choice. The stress relaxation simulations are not only computationally much more expensive, but the evaluation of the results suffers from the uncertainty in the choice of damping function.

For most of the polymers, we observed excellent agreement between the PPA predicted plateau moduli and the experimental values. Five out of eight polymer models were within 5% and the remaining three being within 30% of the experimental plateau moduli. We observed the largest deviations for PE298. They are comparable to those reported for another bead-spring model of PE,¹² while evaluating the proper PPA measures⁷⁷ for atomistic models appears to reproduce experimental entanglement moduli.¹¹⁶ Drawing on the analogy to entanglements in θ -solutions,^{68,117} we can only speculate that details in the local packing or the different bending angle *distributions* modify the entanglement density in the present KG model relative to the experimental target system. The problems might be particularly pronounced for PE298, which has with $n_K = 9.15$ the highest reduced Kuhn density of all investigated systems (Table 2) and is thus closest to the crossover to the tightly entangled regime expected around $n_K \approx \alpha = 20$.⁶⁸

Computationally the KG models are very cheap compared to atomistic detailed simulations. Based on our time mapping of polymer dynamics, we have estimated that the KG models are 10^5 times faster than atomistic models for PI and PDMS. For systems close to the glass transition, the speedup in modelling the large scale behaviour along the present lines would be exponentially larger. Compared to an atomistic model, this obviously comes at the price of loosing the ability to *predict* any of the glassy behaviour. In terms of computational effort, we have studied melts of $2 - 8 \times 10^6$ beads with about 100 entanglements per chain. For each of the systems studied, the equilibration procedure took less than 1000 core hours. The primitive path analysis required less than 20 core hours. Finally the deformation and subsequent stress relaxation required about 30000 node hours.

The present coarse-graining level is about one bead per chemical monomer, or two to three beads per Kuhn segment. It results from matching the Kuhn length and reduced Kuhn segment density, and is not directly adjustable except by changing the equilibrium bond length of the KG model or the density of beads. Here we have chosen to keep these at their standard KG values. Hence there are a number of future avenues for improving and accelerating the dynamics. Alternatively, the number of beads per Kuhn unit could be reduced by using rods rather than beads as

the fundamental build blocks of coarse-grained models.

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References

- (1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca N.Y, 1953.
- (2) Flory, P. J. *Statistical Mechanics of Chain Molecules*; 1969.
- (3) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Claredon Press: Oxford, 1986.
- (4) de Gennes, P.-G. *Scaling concepts in polymer physics*; Cornell University Press: New York, 1979.
- (5) Peter, C.; Kremer, K. *Faraday Discuss.* **2010**, *144*, 9.
- (6) Binder, K. *Monte Carlo and Molecular Dynamics simulations in polymer science*; Oxford University Press New York, 1995; Vol. 95.
- (7) Kremer, K. In *Soft and Fragile Matter: Non Equilibrium Dynamics, Metastability And Flow.*; Cates, M. E., Evans, M. R., Eds.; J. W. Arrowsmith Ltd.: Bristol, U.K., 2000; p 145.
- (8) Kremer, K. *Macromol. Chem. Phys.* **2003**, *204*, 257.
- (9) Müller-Plathe, F. *Soft Mater.* **2002**, *1*, 1.
- (10) Müller-Plathe, F. *Chem. Phys. Chem.* **2002**, *3*, 754.
- (11) Sun, Q.; Faller, R. *Comput. Chem. Eng.* **2005**, *29*, 2380.

- (12) Tzoumanekas, C.; Theodorou, D. N. *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 61.
- (13) Peter, C.; Kremer, K. *Soft Matter* **2009**, *5*, 4357.
- (14) Li, Y.; Abberton, B. C.; Kröger, M.; Liu, W. K. *Polymers* **2013**, *5*, 751.
- (15) Karayiannis, N. C.; Giannousaki, A. E.; Mavrantzas, V. G.; Theodorou, D. N. *J. Chem. Phys.* **2002**, *117*, 5465.
- (16) Karayiannis, N. C.; Giannousaki, A. E.; Mavrantzas, V. G. *J. Chem. Phys.* **2003**, *118*, 2451.
- (17) Peristeras, L. D.; Economou, I. G.; Theodorou, D. N. *Macromolecules* **2005**, *38*, 386.
- (18) Faller, R.; Müller-Plathe, F.; Doxastakis, M.; Theodorou, D. *Macromolecules* **2001**, *34*, 1436.
- (19) Faller, R.; Müller-Plathe, F. *Polymer* **2002**, *43*, 621.
- (20) Faller, R.; Reith, D. *Macromolecules* **2003**, *36*, 5406.
- (21) Li, Y.; Kröger, M.; Liu, W. K. *Polymer* **2011**, *52*, 5867.
- (22) Harmandaris, V.; Adhikari, N.; van der Vegt, N. F.; Kremer, K. *Macromolecules* **2006**, *39*, 6708.
- (23) Chen, X.; Carbone, P.; Cavalcanti, W. L.; Milano, G.; Müller-Plathe, F. *Macromolecules* **2007**, *40*, 8087.
- (24) Karimi-Varzaneh, H. A.; Carbone, P.; Müller-Plathe, F. *Macromolecules* **2008**, *41*, 7211.
- (25) Eslami, H.; Karimi-Varzaneh, H. A.; Müller-Plathe, F. *Macromolecules* **2011**, *44*, 3117.
- (26) Heine, D. R.; Grest, G. S.; Lorenz, C. D.; Tsige, M.; Stevens, M. J. *Macromolecules* **2004**, *37*, 3857.
- (27) Economou, I. G.; Makrodimitri, Z. A.; Kontogeorgis, G. M.; Tihic, A. *Mol. Simul.* **2007**, *33*, 851.

- (28) Doherty, D.; Holmes, B.; Leung, P.; Ross, R. *Comput. Theor. Polym. S.* **1998**, *8*, 169.
- (29) Chen, C.; Depa, P.; Maranas, J. K.; Sakai, V. G. *J. Chem. Phys.* **2008**, *128*, 124906.
- (30) Tschöp, W.; Kremer, K.; Batoulis, J.; Bürger, T.; Hahn, O. *Acta. Polym.* **1998**, *49*, 61.
- (31) Abrams, C. F.; DelleSite, L.; Kremer, K. In *Bridging Time Scales: Molecular Simulations for the Next Decade*; Mareschal, M., Ciccotti, G., Eds.; Springer: Berlin, Heidelberg, 2002.
- (32) Abrams, C. F.; Kremer, K. *Macromolecules* **2003**, *36*, 260.
- (33) Hess, B.; León, S.; Van Der Vegt, N.; Kremer, K. *Soft Matter* **2006**, *2*, 409.
- (34) Tsolou, G.; Mavrantzas, V. G.; Theodorou, D. N. *Macromolecules* **2005**, *38*, 1478.
- (35) Strauch, T.; Yelash, L.; Paul, W. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1942.
- (36) Milano, G.; Müller-Plathe, F. *J. Phys. Chem. B.* **2005**, *109*, 18609.
- (37) Karayiannis, N. C.; Mavrantzas, V. G.; Theodorou, D. N. *Macromolecules* **2004**, *37*, 2978.
- (38) Neyertz, S.; Brown, D. *Macromolecules* **2008**, *41*, 2711.
- (39) Carbone, P.; Varzaneh, H. A. K.; Chen, X.; Müller-Plathe, F. *J. Chem. Phys.* **2008**, *128*, 064904.
- (40) Sukumaran, S. K.; Grest, G. S.; Kremer, K.; Everaers, R. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 917.
- (41) Wittmer, J. P.; Meyer, H.; Baschnagel, J.; Johner, A.; Obukhov, S.; Mattioni, L.; Müller, M.; Semenov, A. N. *Phys. Rev. Lett.* **2004**, *93*, 147801.
- (42) Grest, G. S.; Kremer, K.; Milner, S. T.; Witten, T. A. *Macromolecules* **1989**, *22*, 1904.
- (43) Grest, G. S.; Kremer, K. *Macromolecules* **1990**, *23*, 4994.
- (44) Duering, E. R.; Kremer, K.; Grest, G. S. *Phys. Rev. Lett.* **1991**, *67*, 3531.

- (45) Duering, E. R.; Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1994**, *101*, 8169.
- (46) Murat, M.; Grest, G. *Macromolecules* **1991**, *24*, 704.
- (47) Murat, M.; Grest, G. S. *Phys. Rev. Lett.* **1989**, *63*, 1074.
- (48) Grest, G. S.; Murat, M. In *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*; Binder, K., Ed.; Oxford University Press: New York, 1995; p 476.
- (49) Grest, G. S. *Phys. Rev. Lett.* **1996**, *76*, 4979.
- (50) Aoyagi, T.; Takimoto, J.-i.; Doi, M. *J. Chem. Phys.* **2001**, *115*, 552.
- (51) Gersappe, D. *Phys. Rev. Lett.* **2002**, *89*, 058301.
- (52) Pierce, F.; Perahia, D.; Grest, G. S. *Macromolecules* **2009**, *42*, 7969.
- (53) Yagyu, H.; Utsumi, T. *Comput. Mater. Sci.* **2009**, *46*, 286.
- (54) Sussman, D. M.; Tung, W.-S.; Winey, K. I.; Schweizer, K. S.; Riggleman, R. A. *Macromolecules* **2014**, *47*, 6462.
- (55) Ge, T.; Robbins, M. O.; Perahia, D.; Grest, G. S. *Phys. Rev. E* **2014**, *90*, 012602.
- (56) Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1990**, *92*, 5057.
- (57) Kröger, M. *Phys. Rep.* **2004**, *390*, 453.
- (58) Faller, R.; Kolb, A.; Müller-Plathe, F. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2071.
- (59) Faller, R.; Müller-Plathe, F.; Heuer, A. *Macromolecules* **2000**, *33*, 6602.
- (60) Faller, R.; Müller-Plathe, F. *Chem. Phys. Chem.* **2001**, *2*, 180.
- (61) Kröger, M.; Hess, S. *Phys. Rev. Lett.* **2000**, *85*, 1128–1131.
- (62) Aoyagi, T.; Doi, M. *Comput. Theor. Polym. S.* **2000**, *10*, 317.

- (63) Everaers, R.; Kremer, K. *J. Mol. Mod.* **1996**, *2*, 293.
- (64) Everaers, R.; Kremer, K. *Phys. Rev. Lett.* **1999**, *82*, 1341.
- (65) Grest, G. S.; Kremer, K. *Phys. Rev. A* **1986**, *33*, 3628.
- (66) Svaneborg, C.; Karimi-Varzaneh, H. A.; Hojdis, N.; Everaers, R. Multiscale approach to equilibrating model polymer melts. Submitted to *Phys. Rev. E*. 2016.
- (67) Everaers, R.; Sukumaran, S. K.; Grest, G. S.; Svaneborg, C.; Sivasubramanian, A.; Kremer, K. *Science* **2004**, *303*, 823–826.
- (68) Uchida, N.; Grest, G. S.; Everaers, R. *J. Chem. Phys.* **2008**, *128*, 044902.
- (69) Witten, T. A.; Milner, S. T.; Wang, Z.-G. In *Multiphase Macromolecular Systems*; Culbertson, B., Ed.; Plenum Press New York, 1989.
- (70) Fetters, L. J.; Lohse, D. J.; Milner, S. T.; Graessley, W. W. *Macromolecules* **1999**, *32*, 6847.
- (71) Rouse Jr, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
- (72) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *91*, 513.
- (73) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1023.
- (74) Lin, Y.-H. *Macromolecules* **1987**, *20*, 3080.
- (75) Kavassalis, T. A.; Noolandi, J. *Phys. Rev. Lett.* **1987**, *59*, 2674.
- (76) Rosa, A.; Everaers, R. *Phys. Rev. Lett.* **2014**, *112*, 118302.
- (77) Everaers, R. *Phys. Rev. E* **2012**, *86*, 022801.
- (78) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.

- (79) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
- (80) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
- (81) McLeish, T. C. B. *Adv. Phys.* **2002**, *5*, 1379.
- (82) Rottler, J.; Barsky, S.; Robbins, M. O. *Phys. Rev. Lett.* **2002**, *89*, 148304.
- (83) Rottler, J.; Robbins, M. O. *Phys. Rev. E.* **2003**, *68*, 011801.
- (84) Rosa, A.; Everaers, R. *PLoS. Comput. Biol.* **2008**, *4*, e1000153.
- (85) Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. *J. Chem. Phys.* **2011**, *134*, 204904.
- (86) Rosa, A.; Becker, N. B.; Everaers, R. *Biophys. J.* **2010**, *98*, 2410.
- (87) Grønbech-Jensen, N.; Farago, O. *Mol. Phys.* **2013**, *111*, 983.
- (88) Grønbech-Jensen, N.; Hayre, N. R.; Farago, O. *Comp. Phys. Comm.* **2014**, *185*, 524.
- (89) Plimpton, S. *J. Comput. Phys.* **1995**, *117*, 1.
- (90) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
- (91) Wittmer, J. P.; Beckrich, P.; Johner, A.; Semenov, A. N.; Obukhov, S. P.; Meyer, H.; Baschnagel, J. *Europhys. Lett.* **2007**, *77*, 56003.
- (92) Wittmer, J. P.; Beckrich, P.; Meyer, H.; Cavallo, A.; Johner, A.; Baschnagel, J. *Phys. Rev. E.* **2007**, *76*, 011803.
- (93) Beckrich, P.; Johner, A.; Semenov, A. N.; Obukhov, S. P.; Benoit, H.; Wittmer, J. P. *Macromolecules* **2007**, *40*, 3805.
- (94) Meyer, H.; Wittmer, J. P.; Kreer, T.; Beckrich, P.; Johner, A.; Farago, J.; Baschnagel, J. *Eur. Phys. J. E.* **2008**, *26*, 25.

- (95) Semenov, A. N. *Macromolecules* **2010**, *43*, 9139.
- (96) Daoulas, K. C.; Terzis, A. F.; Mavrantzas, V. G. *Macromolecules* **2003**, *36*, 6674.
- (97) Karayiannis, N. C.; Mavrantzas, V. G.; Theodorou, D. N. *Phys. Rev. Lett.* **2002**, *88*, 105503.
- (98) Hoy, R. S.; Foteinopoulou, K.; Kröger, M. *Phys. Rev. E* **2009**, *80*, 031803.
- (99) Likhtman, A. E.; Sukumaran, S. K.; Ramirez, J. *Macromolecules* **2007**, *40*, 6748.
- (100) Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1990**, *92*, 5057.
- (101) Zhang, G.; Stuehn, T.; Daoulas, K. C.; Kremer, K. *J. Chem. Phys.* **2015**, *142*, 221102.
- (102) Fetters, L. J.; Lohse, D. J.; Colby, R. H. In *Physical properties of polymers handbook*; Mark, J., Ed.; Springer, 2007; p 447.
- (103) Vaca Chávez, F.; Saalwächter, K. *Macromolecules* **2011**, *44*, 1549.
- (104) Auhl, D.; Ramirez, J.; Likhtman, A. E.; Chambon, P.; Fernyhough, C. *J. Rheol.* **2008**, *52*, 801.
- (105) Bennemann, C.; Paul, W.; Binder, K.; Dünweg, B. *Phys. Rev. E* **1998**, *57*, 843.
- (106) Moreira, L. A.; Zhang, G.; Müller, F.; Stuehn, T.; Kremer, K. *Macromol. Theory Simul.* **2015**, *24*, 419.
- (107) Wang, Q. *Soft Matter* **2009**, *5*, 4564.
- (108) Unidad, H. J.; Goad, M. A.; Bras, A. R.; Zamponi, M.; Faust, R.; Allgaier, J.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D.; Fetters, L. J. *Macromolecules* **2015**, *48*, 6638.
- (109) Likhtman, A.; McLeish, T. *Macromolecules* **2002**, *35*, 6332.
- (110) Rubinstein, M.; Panyukov, S. *Macromolecules* **1997**, *30*, 8036.
- (111) Everaers, R. *New J. Phys.* **1999**, *1*, 12.1.

- (112) Mergell, B.; Everaers, R. *Macromolecules* **2001**, *34*, 5675.
- (113) Rubinstein, M.; Panyukov, S. *Macromolecules* **2002**, *35*, 6670.
- (114) Hou, J.-X.; Svaneborg, C.; Everaers, R.; Grest, G. S. *Phys. Rev. Lett.* **2010**, *105*, 068301.
- (115) Svaneborg, C.; Grest, G. S.; Everaers, R. *Phys. Rev. Lett.* **2004**, *93*, 257801.
- (116) Foteinopoulou, K.; Karayiannis, N. C.; Mavrantzas, V. G.; Kröger, M. *Macromolecules* **2006**, *39*, 4207.
- (117) Milner, S. *Macromolecules* **2005**, *38*, 4929.